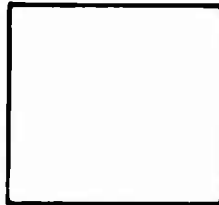


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REPORT

NO. WAL 121/16

Q.O. PROJECT: TD4-121

D/A PROJECT: 593-05-023

COOPERATIVE ANALYSIS OF NATIONAL BUREAU OF STANDARDS
STANDARD SAMPLE NO. 30a

BY

E. F. JACOBSON

DATE 10 April 1956

WATERTOWN ARSENAL
WATERTOWN, MASS.

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WAL 121/16

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**COOPERATIVE ANALYSIS OF NATIONAL BUREAU OF STANDARDS
STANDARD SAMPLE NO. 30e**

by

E. F. JACOBSON

O.O. Project: TD4-121, Ferrous Metals Problems
D/A Project: 593-08-023
Memorandum Report No.: WAL 121/16
Filing Title: Chemical Analysis - Analysis of
Standard Sample No. 30e (Cr-V)

**WATERTOWN ARSENAL
WATERTOWN 72, MASS.**

WATERTOWN ARSENAL LABORATORIES

10 April 1956

TITLE

COOPERATIVE ANALYSIS OF NATIONAL BUREAU OF STANDARDS
STANDARD SAMPLE NO. 30e (Cr-V STEEL)

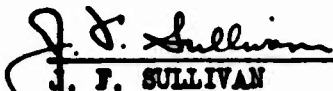
ABSTRACT

An exacting analysis was made of chromium-vanadium steel for the National Bureau of Standards in conjunction with their certification program for standard steels. The Watertown Arsenal Laboratories' results were satisfactory to the National Bureau of Standards and have been incorporated by them in a certificate of analysis for Standard Steel No. 30e.


SUMMARY

The Watertown Arsenal Laboratories have analysed Standard Sample No. 30e for ten elements. In general, the standard methods of analysis in use at the Analytical Chemistry Branch of the Watertown Arsenal Laboratories were employed. A brief outline of the methods of analysis is given, and a copy of the final certificate of analysis furnished by the National Bureau of Standards is attached (Appendix A).

APPROVED:


J. F. SULLIVAN
Associate Technical Director
Watertown Arsenal Laboratories


E. F. JOHNSON
Supervisory Physical
Science Aide


RUSSELL F. SCOTT, Jr.
Major, Ord Corps
Director
Watertown Arsenal Laboratories

INTRODUCTION

The National Bureau of Standards' Standard Samples are materials which have been carefully analyzed or the physical properties of which have been precisely determined at the Bureau and in some cases, in other laboratories. Today more than 500 different Standard Samples of metals, ores, ceramics, chemicals, as well as reference standards, are available for distribution to analytical and research laboratories.

In connection with the certification of NBS Standard Steel Sample No. 30e, the National Bureau of Standards requested the Analytical Chemistry Branch of the Watertown Arsenal Laboratories to analyze this sample (Appendix B). The sample was subjected to a careful and exacting analysis and the results (Table I) were reported to the National Bureau of Standards, together with a description of the analytical procedures employed. A letter received in reply from the National Bureau of Standards, stated in part: "All your results, with the exception of vanadium, are in good agreement with the other values we have received to date on this standard. Your vanadium value is slightly outside the close limits we like to use for standard samples and we would like you to check this element at your convenience."

Additional work was done on the determination of vanadium, and the results were reported to the National Bureau of Standards. These results, together with the results of the determinations previously submitted, were incorporated in the final certificate of analysis issued by the National Bureau of Standards.

ANALYTICAL METHODS EMPLOYED

Carbon

Apparatus and Reagents

- | | |
|---------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Furnace | - Burrell Electric Furnace, heated to 2050°F with Globar heating elements. |
| Boats | - Johnson, clay boats, 4 3/4" x 5/8", lined with 90-mesh Alundum. |
| Oxygen Purification Train | - The oxygen is bubbled through a tower containing a 50 percent potassium hydroxide solution to remove carbon dioxide, and is then dried by passing through a tower containing silica gel. |
| Combustion Tube | - McDanel Zircotube, packed with finely divided, ironized asbestos to remove dust and oxides of sulfur. |

- Drier - A tube containing anhydrous magnesium perchlorate.
- Absorption Bulb - Nesbitt, filled with Ascarite and magnesium perchlorate to absorb carbon dioxide.
- Accelerator - Granulated tin, 30-mesh.

Procedure

Boats were preburned for 10 minutes and stored in a desiccator. Before using, the preburned boats were lined with alundum and again burned for 10 minutes. A sample weighing 1.3636g was placed in the boat and about 0.2g of granulated tin added as an accelerator. The sample was given a two-minute preheat and burned for eight minutes in a current of oxygen flowing at a rate of about 500 ml per minute. The blank was determined by running a standard sample, with approximately the same percentage of carbon as the unknown, by the same method.

On preliminary runs the average was 0.5164C, but after degreasing the sample by washing the chips with ethyl ether, the percent carbon dropped to 0.510; this showed that the sample was slightly contaminated.

Molybdenum

After solution of a 0.0500g sample in perchloric acid and reduction of ferric iron with stannous chloride, sodium thiocyanate was added to develop the molybdenum thiocyanate complex. The transmittancy of the unextracted solution was then measured at 460mμ with a Coleman 10S spectrophotometer and the concentration of molybdenum determined by reference to a calibration curve based on standard steels. The method was that of Murray and Vigo⁹.

Phosphorus

Two methods for determining phosphorus were employed:

Method A - The alkalimetric method described by Lundell, Hoffman, and Bright⁴:

A two-gram sample was dissolved in nitric acid, the phosphorus precipitated as ammonium phosphomolybdate, filtered, and the precipitate titrated with a solution of sodium hydroxide which had been standardized against standard steels. A modification proposed by Lundell, Hoffman and Bright for alloy steels uses ferrous sulfate and sulfurous acid. This modification was not followed since previous experience at Watertown Arsenal Laboratories had indicated that it gave high and erratic results.

Method B - The alkalimetric method of the ASTM²:

A two-gram sample was dissolved in perchloric acid, fumed, and the phosphorus precipitated as the phosphomolybdate and finished as above. Filtration of the sample after fuming and treatment of the solution with potassium permanganate and sulfurous acid, as recommended by the ASTM, has not been found necessary and was not done.

Sulfur

Determination of sulfur was made by both evolution and combustion methods:

Method A - The evolution method used was that described by Lundell, Hoffman and Bright⁵. A five-gram sample of steel was dissolved in hydrochloric acid and the evolved hydrogen sulfide was reacted with cadmium chloride to form cadmium sulfide, which was titrated with an iodate solution. The iodate solution was standardized against potassium dichromate through sodium thiosulfate solution.

Method B - The combustion method was similar to that employed by the ASTM for stainless steels⁵. The furnace, a Dietert electric furnace with Globar heating elements, was heated to 2600°F. The titrating solution was standardized against standard steels.

Silicon .

Silicon was determined on a 4.672-g sample by double dehydration with perchloric acid and volatilization with hydrofluoric acid. A blank was determined on the reagents and used to correct the silicon value. The method used followed closely the procedure of Lundell, Hoffman, and Bright⁶.

Nickel

A four-gram sample was dissolved in hydrochloric acid and the solution was oxidized with nitric acid. After the addition of tartaric acid and neutralization with ammonia the nickel was precipitated with an alcoholic solution of dimethylglyoxime. After standing at room temperature for 20 hours the precipitate was filtered through a tared, fritted-glass crucible, dried at 130°C for two hours, and weighed.

Manganese

The persulfate oxidation as recommended by the ASTM¹ was the method which was finally used and which provided the submitted results. A one-gram sample was dissolved in sulfuric and phosphoric acids, and the manganese was oxidized with ammonium persulfate in the presence of silver nitrate. The permanganic acid was reduced with an arsenite solution which had been standardized against standard steels.

Preliminary determinations were made by the Watertown Arsenal Laboratories' method, which is very similar to the ASTM method except that a smaller sample weight, 0.200g, is used. Twenty-two runs averaged 0.796 percent manganese.

A number of determinations were made after a preliminary separation with zinc oxide to remove the chromium, which is usually considered to interfere with the final titration. Fourteen runs averaged 0.795 percent manganese.

Chromium

A two-gram sample was dissolved in sulfuric and phosphoric acids, and the chromium was determined by ammonium persulfate oxidation and titration with excess ferrous ammonium sulfate and potassium permanganate.

The potassium permanganate solution was standardized against sodium oxalate and checked with standard steels of composition similar to the unknown.

The method was that described by Lundell, Hoffman, and Bright⁷.

Copper

Ten-gram samples of Sample 30e and of standard samples of similar composition were analyzed together. The samples were dissolved in dilute sulfuric acid (1:9) and the copper was precipitated with sodium thiosulfate solution. After solution of the precipitate, the copper was separated from the iron and chromium with ammonia. The copper was determined gravimetrically by electrolysis of the solution. The results on the standard samples were low and erratic, due presumably to co-precipitation of copper with iron and chromium.

Copper determinations on another set of standard samples, incorporating a double precipitation of iron and chromium with ammonia to recover co-precipitated copper, showed good agreement with the certificate values for copper.

Vanadium

Method A - This method utilized the solution remaining after the chromium determination, according to the method described by Lundell, Hoffman, and Bright⁸. The vanadium was reduced with ferrous ammonium sulfate, the solution treated with ammonium persulfate and titrated with standard potassium permanganate solution. The results were in good agreement, and were reported to the National Bureau of Standards.

Method B - It was also desired to determine vanadium by a direct method. Therefore, Pigott's¹⁰ method using sodium fluoride, urea, and

diphenylamine sulfonate was tried. The results obtained from the known standards were low and erratic, and were not reported.

Method C - This was the same as Method A. except that four-gram samples were taken. Since the amount of vanadium found in standard samples by this method was about 0.004 percent too high, the following methods (D, E, and F) were tried.

Method D - This method employed a cupferron separation of vanadium from a ten-gram sample followed by perchloric acid oxidation. This method yielded low and erratic results on standard samples.

Method E - Potentiometric titration of vanadium was unsuccessful because of inadequate instrumentation.

Method F - This method employed a bicarbonate separation of vanadium from a ten-gram sample, and oxidation with ammonium persulfate in the presence of silver nitrate. The titration was performed as described in Method A. This method gave good results on standard samples and was applied to the determination of vanadium in 30e when the National Bureau of Standards requested a recheck of the vanadium. A new set of values based on this method was reported to the National Bureau of Standards. Their reply indicated excellent agreement of this set with their tentative value for vanadium.

REFERENCES

1. A. S. T. M. Methods for Chemical Analysis of Metals, p. 82, 1950.
2. Ibid., p. 89, section 39b.
3. Ibid., p. 130
4. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," Wiley and Sons, New York, p. 223, 1931.
5. Ibid., p. 238
6. Ibid., p. 261
7. Ibid., p. 291
8. Ibid., p. 308
9. Murray, K., and Vigo, S., "Determination of Molybdenum in Alloy Steels and Cast Irons," Memorandum Report No. WAL 310/52, 1945.
10. Pigott, E. C., "Ferrous Analysis-Modern Practice and Theory," Wiley and Sons, New York, Ed. 2, p. 302, 1953.

TABLE I
ANALYTICAL RESULTS

	<u>PERCENT FOUND</u>			<u>AVERAGE</u>	<u>CERTIFICATE VALUE</u>
Carbon	0.508 .510 .504 .506 .508	0.510 .510 .512 .510	0.512 .512 .512 .510	0.510	0.505
Manganese	0.794 .792 .792 .788	0.792 .791 .790 .790	0.788 .793 .792 .792	0.791	0.786
Phosphorus Method A	0.025 .024 .024 .024	0.024 .024 .024 .023	0.024 .023	0.024	0.026
Method B	0.025 0.025	0.024 0.024		0.025	0.026
Sulfur Method A	0.036 .036 .034 .035	0.035 .036 .035 .035	0.035 0.035	0.036	0.036
Method B	0.034 .034 .032	0.033 0.034 0.035		0.034	0.036
Silicon	0.268 .265 .266	0.265 0.267 0.265		0.266	0.269
Copper	0.091 .092 .090	.091 .092 .092		0.091	.094
Nickel	0.023 .024 .023	.023 .023 .025		0.024	0.027
Chromium	0.937 .937 .937	.940 .935 .935	.940 .937 .935	0.937	0.934
Vanadium Method A	0.15 .16 .16	0.16 .16 .15	0.15 .16 .16	0.16	0.149
Method F	0.146 .148 .148	0.148 .148 .148		0.148	0.149
Molybdenum	0.008 .008 .008	0.008 .008 .008		0.008	0.007

APPENDIX A
UNITED STATES DEPARTMENT OF COMMERCE
WASHINGTON

National Bureau of Standards

Certificate of Analyses

Standard Sample 30E

Chromium-Vanadium Steel

ANALYST	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo	N				
	Direct combustion	Bismuthate (FeSO ₄ -KMnO ₄)	Permanganate-Arsenite	Gravimetric (weighed as Mg ₂ P ₂ O ₇ after removal of arsenic)	Alkali-Molybdate *	Gravimetric (direct oxidation and precipitation after reduction of iron)	Combustion	Evolution with HCl (1-1) ZnS-Iodine (theoretical sulfur titer) *	Perchloric acid dehydration	H ₂ S-CuS-CuO	Weighted as nickel dimethylglyoxime	Permanganate oxidation (FeSO ₄ -KMnO ₄ titration)	HNO ₃ oxidation, potentiometric titration	Photometric	Distillation-titration
1	0.501		0.783	0.028	* 0.026	0.036	* 0.036	0.037	* 0.273	* 0.092	0.027	* 0.936	0.148	0.007	* 0.007
2	.508		.795	.027	.027	.034	.035	.034	.271	.091	.026	.932	.146	.009	
3	.506		* .778	.028		.037	* .037	* .264	* .094	* .026	.939	* .147	.008		
4	.506		* .793	.024	.026	.036	.037	.035	.264	* .096	* .027 { .935 } * .939	.152	.006		
5	.505		.790		{ .026 } * .025		.035		.274	* .10	.026	.933	* .148	.007	
6	.506		.778		.028		* .037	.037	.269 { .092 } * .091		.026	.933	* .150	.007	
7	.506		.780	.027			* .037	* .269	* .099	* .028	.933	* .147	.007		
8	.503	* .789	.787		.024	.035	.036		* .270	.092	.029	.932	* .150	.007	
9	.502		.788	.026		.033			* .269	.092	* .028	* .929	* .152	* .005	
10	.510		.791		.024		.034	* .035	* .266	* .091	.024	.937	* .148	.008	
Average	0.505	0.789	0.786	0.028	0.026	0.035	0.036	0.036	0.269	0.094	0.027	0.934	0.149	0.007	
General % average	0.505	0.786		0.026		0.036			0.269	0.094	0.027	0.934	0.149	0.007	

* Precipitated at 40° C, washed with a 1-percent solution of KNO_3 and titrated with alkali standardized by the use of acid potassium phthalate and the ratio 21NaOH:1P.

* Values obtained by standardizing the titrating solution by means of sodium oxalate through KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_8$ and use of the ratio 21:18.

* Methylred-m-blue photometric method. See J. Research NBS 25, 685 (1941) RP1386.

* 2 g sample burned in oxygen at 1425° C and sulfur dioxide absorbed in starch-iodine solution. Iodine liberated from iodide by titration, during the combustion, with standard KIO_3 solution. Titer based on 93 percent of the theoretical factor.

* Double dehydration with H_2SO_4 with intervening filtration.

* Diethylthiocarbamate photometric method. See J. Research NBS 47, 340 (1951) RP2265.

* Potentiometric titration with $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$.

* Sulfuric acid digestion for 4 hours of 0.5g-sample. See J. Research NBS 43, 201 (1949) RP2021.

* Titrating solution standardized with a standard steel.

* Sulfur case absorbed in neutral H_2O_2 and titrated with NaOH .

* Double dehydration.

* Finished by electrolysis.

* Vanadium separated from iron by precipitation as the phosphovanadate, and determined by the $\text{KMnO}_4\text{-(NH}_4)_2\text{S}_2\text{O}_8$ method.

* $\text{H}_2\text{S-MoO}_3\text{-MoO}_3$.

* Chromium volatilized as CrOCl_2 .

* Absorbed in ammoniacal cadmium chloride.

* Dimethylglyoxime precipitate titrated with cyanide.

* Vanadium titrated with KMnO_4 after addition of K_2HPO_4 .

* Chromium removed by precipitation with ZnO .

* Copper-ammonia complex-photometric method.

* Perchloric acid oxidation.

* $\text{FeSO}_4\text{-(NH}_4)_2\text{C}_2\text{O}_4\text{-KMnO}_4$ method.

* Dimethylglyoxime-photometric method.

* H_2O_2 -photometric method.

* Titration with sodium arsenite.

* Vanadium precipitated with cupferron, oxidized with perchloric acid and titrated with $\text{FeO}_2\text{-KMnO}_4$.

* Alpha-benzamidine method.

List of Analysts

1. Ferrous Laboratory, National Bureau of Standards. Analysis by J. I. Shultz, H. Jacobson and L. Machlan.
2. O. W. Baldwin, Chief Chemist, United States Steel Corporation, Gary Steel Works, Gary, Ind.
3. E. B. Burger, United States Steel Corporation, Homestead District Works, Homestead, Pa.
4. W. W. Clarke, Latrobe Steel Company, Latrobe, Pa.
5. J. E. Spittle, Ford Motor Company, Dearborn, Mich.
6. C. H. Cramer, United Engineering and Foundry Company, Vandergrift, Pa.

7. C. H. Fitzwilson, United States Steel Corporation, Columbia-Geneva Steel Division, San Francisco, Calif.
8. R. F. Lab and A. C. Hale, Copperweld Steel Company, Warren, Ohio.
9. F. J. Cloan, Crucible Steel Company of America, Midland Works, Midland, Pa.
10. S. Vigo and E. F. Jacobson, Watertown Arsenal, Watertown, Mass.

The steel for the preparation of this standard was furnished by the United States Steel Corporation.
WASHINGTON, D. C., March 15, 1955.

A. V. ASTIN, Director.

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APPENDIX B

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
December 30, 1953

In your reply
Refer to File
No. 5.4

Mr. S. Vigo, Chemical Laboratory
Watertown Arsenal
Watertown, Massachusetts

Subject: Cooperative Analysis of NBS Chromium-Vanadium
Steel, 30e.

Dear Mr. Vigo:

Under separate cover we are forwarding you a portion of NBS Standard Chromium-vanadium steel 30e. We ask the cooperation of your laboratory in the analysis of this steel for carbon, manganese, phosphorus, sulfur, silicon, copper, nickel, chromium, vanadium and molybdenum. Values for sulfur by the evolution method should be based on the theoretical titre (for example, through potassium dichromate or sodium oxalate) instead of a standard steel or iron.

The National Bureau of Standards will furnish to cooperating analysts, free of charge and upon request, any NBS Standard Samples they may wish to use in the work. A list of these standards is enclosed. Please note that standard 30d is out of stock, and cannot be furnished.

If convenient, we would like to have reports by February 20. Please include with your report a brief outline of the methods employed. These should include (1) weights of sample, (2) all steps of the method, (3) method of standardizing each volumetric or photometric method, and (4) for carbon (a) the blank (g. of CO₂) and (b) the temperature of the combustion operation. The carbon values reported should be the net value. To aid our records on the accuracy obtained in chemical analysis, it is desired that the results of all individual determinations be reported, except when known sources of errors such as spills or faulty endpoints are encountered. If a number of runs were made at different times by the same or different analysts, please indicate by grouping the results as set 1 (operator A): set 2 (operator A or B) etc.

Will you please advise whether you will be able to cooperate in the analysis of this standard.

Very truly yours,

Enclosure

sst/ John L. Hague, Assistant
Chief
Analytical Chemistry Section
Division of Chemistry

B-1

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